

Complexation of Titanium(IV) with 4-Nitrocatechol and Tetrazolium Salts Tetrazolviolet and Iodonitrotetrazolium Chloride

S. KOSTOVA*, A. DIMITROV, and A. ALEXANDROV

*Department of General and Inorganic Chemistry, University of Ploudiv,
4000 Ploudiv, Bulgaria*

Received 19 February 1999

The extraction of the ion-associates of titanium(IV) with 4-nitrocatechol and the tetrazolium salts tetrazolviolet and iodonitrotetrazolium chloride has been studied. The optimum extraction conditions and the effect of diverse ions have been established. The mole ratio between Ti(IV), 4-nitrocatechol, and tetrazolium salts was 1:2:2. Beer's law was obeyed over the range of 0.172—2.044 $\mu\text{g cm}^{-3}$ for ion association complex with iodonitrotetrazolium chloride (INT), and 0.20—2.00 $\mu\text{g cm}^{-3}$ with tetrazolviolet (TV). The molar absorption coefficients (ϵ) observed are: for the ion-associate with INT $2.38 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $\lambda = 430 \text{ nm}$ and for the associate with TV $4.40 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $\lambda = 440 \text{ nm}$. The ion-associates were applied to extraction-spectrophotometric determination of titanium in aluminium alloys.

It is known that *ortho*-dihydroxy derivatives of benzene form chelate complexes with a number of ions. The application of their nitro- and bromosubstituted derivatives, however, is more favourable because of their stability against oxidation and the formation of complex compounds with intense colour.

4-Nitrocatechol (2,3-dihydroxy-4-nitrobenzene) has acid-base properties [1]. Like the other nitro derivatives of dihydroxybenzene (3-nitro-, 3,4-dinitro-, and 3,5-dinitrobenzene), it forms complexes with Ge(IV), V(V), B(III), and Sn(IV) [2—7]. The addition of organic dyes leads to the increase in the sensitivity of colour reactions [3, 8, 9]. It has been established that niobium(V), tungsten(VI), and germanium(IV), in the presence of 4-nitrocatechol, form ion association complexes (IAC) with tetrazolium salts (TS) which are readily soluble in organic solvents [10—14]. In a previous work we have studied the formation of the IAC of titanium(IV) with 4-nitrocatechol (NC) and 2,3,5-triphenyltetrazolium chloride, and its extraction in organic solvents [15].

The use of tetrazolium salts with more complex substitutes in the tetrazolium ring usually leads to an improvement of the properties of the ion-associates obtained [16].

The present work is a study of the reaction of titanium(IV) with 4-nitrocatechol and the tetrazolium salts 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride (iodonitrotetrazolium chloride, INT) and 2,5-diphenyl-3-(1-naphthyl)-2*H*-tetrazolium chloride (tetrazolviolet, TV), as well as a study of the formation of ion association complexes in aque-

ous medium, their extraction in organic solvents and their application in the analytical practice.

EXPERIMENTAL

All the chemicals used were of anal. grade. The solution of titanium(IV) of the final concentration $c(\text{TiO}_2) = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ was prepared from 0.5030 g of TiO_2 preliminarily heated up to 900°C. 28 cm^3 of concentrated H_2SO_4 and 12.5 g of $(\text{NH}_4)_2\text{SO}_4$ were then added and the mixture was heated for 4—5 h. After cooling, the resulting solution was transferred into a 250 cm^3 calibrated flask containing 150 cm^3 of water and diluted up to the mark with distilled water. The acidity was determined titrimetrically. Working solutions of lower concentrations were prepared by dilution before use because at $\text{pH} < 2$ titanium(IV) hydrolyzes [17, 18]. The other solutions used had the concentration $c(\text{NC}) = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $c(\text{INT}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $c(\text{TV}) = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$. Chloroform distilled at 62—64°C and concentrated sulfuric acid were also used. IR spectra were determined on a Perkin—Elmer 1750 Infrared Fourier Transform Spectrometer (USA). Absorption spectra were recorded with a spectrophotometer Spekol 11 (Germany) and a Perkin—Elmer Lambda-15 UV/VIS spectrophotometer (USA). Measurements of pH were performed with a pH-meter Pracitronic MV 88 (Germany).

Extraction-spectrophotometric study of ion-associates. Aliquots of the titanium solution, of NC and tetrazolium salts were placed into separatory funnels.

*The author to whom the correspondence should be addressed.

The values pH of acidity were adjusted with solution of sulfuric acid and the volume was brought up to 10 cm³ with distilled water. It was then extracted in an equal volume of organic solvent. The equilibrium is usually reached in 10 min but for more reliable results we extracted for 15 min on a shaking machine. After the separation of two phases the organic phase was transferred into a 1 cm cell through filter paper and the absorbance was measured on a spectrophotometer.

Determination of titanium in aluminium alloys. 0.5000 g of aluminium alloy was dissolved with 7 cm³ of H₂SO₄ ($\varphi_r = 1:1$) and 1 cm³ of HCl ($\varphi_r = 1:1$). After the violent reaction was over, the sample was heated on a sand bath until completely dissolved. The cover glass was then washed with hot water and it was heated again for 5 min. After cooling the solution was filtered into a 50 cm³ calibrated flask and was diluted to the mark with distilled water. The acidity was determined titrimetrically [18]. Three portions of 1 cm³ each were taken from the solution and placed into separatory funnels. Portions of 2 cm³ of 0.01 mol dm⁻³ NC, 4 cm³ of 1.25×10^{-3} mol dm⁻³ TV, and 1 cm³ of ascorbic acid ($w_r = 1\%$) are added, if necessary, pH was adjusted to 1.7–1.8 with solution of sulfuric acid. The volume was brought up to 10 cm³ with distilled water and it was extracted with an equal volume of chloroform. After separation, the absorbance of the organic phase was measured at $\lambda = 440$ nm. A blank without titanium ran in parallel.

RESULTS AND DISCUSSION

Absorption Spectra

Preliminary studies showed that the compounds formed could be extracted with dichloroethane and chloroform. For further studies we used chloroform because the phase separation after extraction in this solvent proved easier. The recorded absorption spectra indicate that Ti—NC—INT is an ion-associate – new bands are not observed but only some absorption additivity in the presence of tetrazolium salt. As seen from Fig. 1, the absorption maxima are in the λ -range of 420–440 nm. As optimum wavelength we used $\lambda = 430$ nm for IAC with INT, because at this wavelength the blank absorbs only slightly. The absorption spectra of the Ti—NC—TV were in the same range. The optimum wavelength used was $\lambda = 440$ nm.

Effect of the Acidity on the Extraction

The most important factor influencing the extraction of Ti(IV) as IAC is the acidity of the aqueous phase. Having in mind the complexity of Ti(IV) state in aqueous and water—acid solutions, and the way of preparing the solution in sulfuric acid medium, Ti(IV) is most likely to be present as $[\text{TiO}(\text{SO}_4)_2]^{2-}$ or $[\text{Ti}(\text{OH})_2(\text{SO}_4)_2]^{2-}$ [17, 19]. The maximum extraction

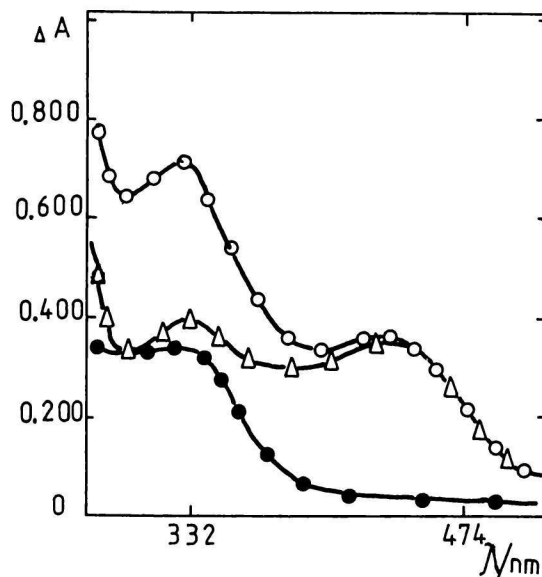


Fig. 1. Absorption spectra in chloroform: Ti—NC—INT (○), reagent blank (●), and the complex *vs.* reagent blank (Δ). pH = 1; $c(\text{Ti}) = 2.5 \times 10^{-5}$ mol dm⁻³; $c(\text{NC}) = 1.4 \times 10^{-4}$ mol dm⁻³; $c(\text{INT}) = 6.0 \times 10^{-4}$ mol dm⁻³.

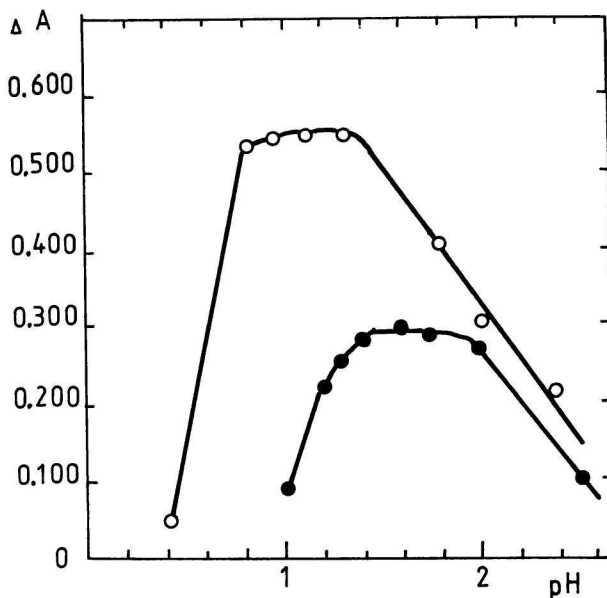


Fig. 2. Relationship between the absorbance of the organic extracts of IAC and pH of aqueous phase. ○ $c(\text{Ti}) = 2.7 \times 10^{-5}$ mol dm⁻³; $c(\text{INT}) = 5.6 \times 10^{-4}$ mol dm⁻³; $c(\text{NC}) = 2.0 \times 10^{-3}$ mol dm⁻³. ● $c(\text{Ti}) = 1.0 \times 10^{-5}$ mol dm⁻³; $c(\text{TV}) = 5.0 \times 10^{-4}$ mol dm⁻³; $c(\text{NC}) = 2.0 \times 10^{-3}$ mol dm⁻³.

of the IAC of Ti(IV) with 4-nitrocatechol and TV can be achieved at a pH in the range of 1.4–1.8, and for IAC with INT at $\text{pH} \cong 1$ (Fig. 2). At $\text{pH} > 4$, the absorbances of the blank are higher, and in strongly acid

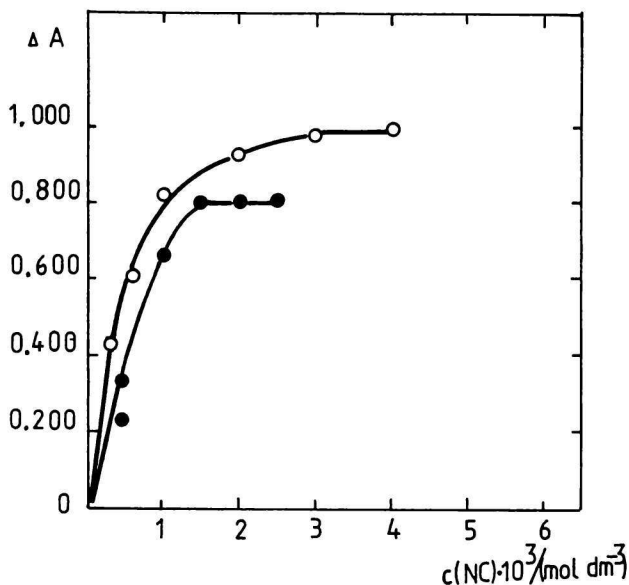


Fig. 3. Absorbance of the organic extracts vs. the concentration of NC plots. \circ $c(\text{Ti}) = 1.86 \times 10^{-5} \text{ mol dm}^{-3}$; $c(\text{TV}) = 3.75 \times 10^{-4} \text{ mol dm}^{-3}$; $\text{pH} = 1.6$. \bullet $c(\text{Ti}) = 3.50 \times 10^{-5} \text{ mol dm}^{-3}$; $c(\text{INT}) = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{pH} = 1.0$.

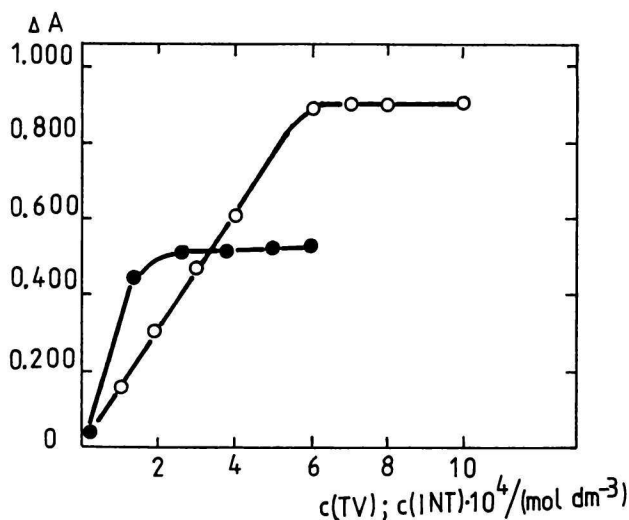


Fig. 4. Absorbance of the organic extracts of IAC vs. concentration of TS plots. \circ $c(\text{Ti}) = 3.7 \times 10^{-5} \text{ mol dm}^{-3}$; $c(\text{NC}) = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{pH} = 1.0$. \bullet $c(\text{Ti}) = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$; $c(\text{NC}) = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$; $\text{pH} = 1.6$.

medium IAC are not extracted. The necessary pH was adjusted with acid of known concentration or with a solution of sodium carbonate and after the extraction it was measured on a pH-meter.

Effect of the Concentration of the Reagents

The complete bonding of titanium(IV) into a chelate complex requires a 40-fold excess of NC for

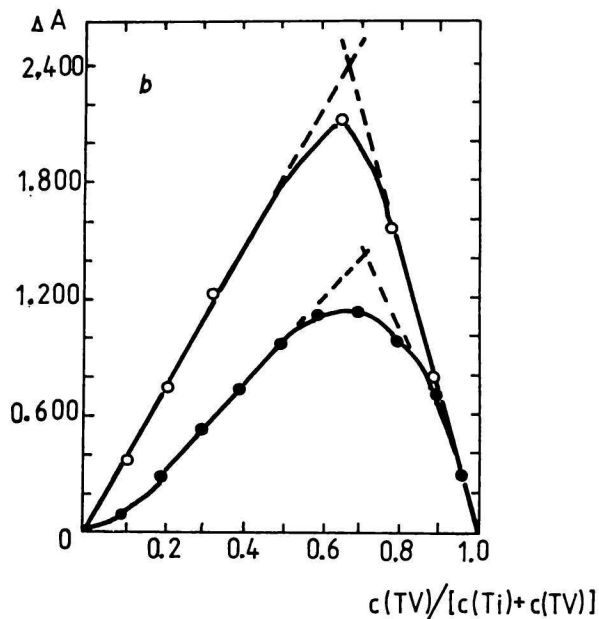
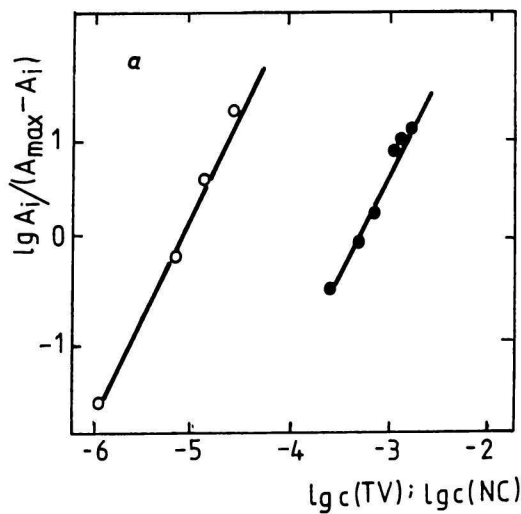


Fig. 5. Determination of the mole ratio between Ti, NC, and TV. a) By the method of the equilibrium shift: \circ $n(\text{Ti}):n(\text{TV})$, \bullet $n(\text{Ti}):n(\text{NC})$. The slope of the curves is 60° which corresponds to a ratio 1:2. b) By the method of continuous variations of $n(\text{Ti}):n(\text{TV})$. The maximum corresponds to a ratio 1:2.

IAC with INT and 200-fold excess for IAC with TV (Fig. 3). For a maximum association and extraction the amount of tetrazolium salts should not be lower than a 20-fold excess for INT and 40-fold excess for TV (Fig. 4).

Beer's Law

To find out the regions of the linear relationship between titanium concentration in aqueous phase and the absorbance in the organic phase after extraction, further studies were carried out using regression analysis. The results are presented in Table 1.

Table 1. Regression Analysis Results according to the Equation $A = \epsilon c b$

Statistical characteristics	Ion association complexes	
	Ti(IV)—NC—INT	Ti(IV)—NC—TV
Linear regression	$3.6 \times 10^{-6} - 43.0 \times 10^{-6} \text{ mol dm}^{-3}$ $(1.72-20.44) \times 10^{-1}/(\mu\text{g cm}^{-3})$	$2.0 \times 10^{-6} - 20 \times 10^{-6} \text{ mol dm}^{-3}$ $(1.00-9.60) \times 10^{-1}/(\mu\text{g cm}^{-3})$
Molar absorption coefficient $\epsilon/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	23800 ± 530	44000 ± 1146
Standard deviation s_r	± 235	± 507

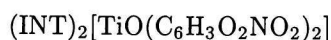
Table 2. Values for the Constants Characterizing the Extraction of the Titanium with 4-Nitrocatechol and Tetrazolium Salts

Ion-associates	k_{ex}	k_{D}	β	$R/\%$
$(\text{INT})_2[\text{TiO}(\text{NC})_2]$	2.40×10^7	5.45	3.7×10^6	84.00
$(\text{TV})_2[\text{TiO}(\text{NC})_2]$	1.33×10^{12}	78.80	1.0×10^{10}	98.74

Composition, Stability, Distribution

According to *Sommer* [6], depending on the acidity of the medium, titanium(IV) forms chelate complexes with pyrocatechol in different mole ratios – from 1:1 to 1:3. By employing the widely used spectrophotometric methods, the method of equilibrium shift and the method of the continuous variations [20], it was established that under optimum extraction conditions the mole ratios, $n(\text{Ti(IV)}):n(\text{NC}):n(\text{TS})$, were 1:2:2 (Fig. 5). The character of the Ti—O bond was studied by IR spectroscopy. The registered spectra for IAC obtained after the evaporation of chloroform extracts showed no bands characteristic of polymer forms. The bands at 975 cm^{-1} are referred to the Ti=O bond, and those at around 700 cm^{-1} to the Ti—O bond [21–23].

On the basis of the studies carried out we propose the following formula for the associates studied



and



The constants needed for the quantitative assessment of the extraction equilibrium were calculated as follows: the extraction constant k_{ex} by the method of *Likussar* and *Boltz* [24], the distribution constant k_{D} and the recovery factor $R/\%$ by comparing the absorption for a single extraction (A_1) to that for triple extraction (A_3) in the equal volumes ($k_{\text{D}} = [\text{Ti}]_{\text{o}}/[\text{Ti}]_{\text{aq}} = A_1/(A_3 - A_1)$); $R/\% = A_1/A_3$; the stability constant β from the equation $\beta = k_{\text{ex}}/k_{\text{D}}$. The values obtained are given in Table 2.

Selectivity

The effect of various ions and reagents on the extraction equilibrium was studied under the optimum extraction conditions. The results are presented in Table 3. As interfering effect we accepted a $\pm 3 \%$ deviation from absorbance of IAC in the absence of a foreign ion.

The results indicate that with respect to both associates and various ions the selectivity is different. The interfering action of Nb(V), Mo(VI), W(VI), and V(V) is due to the formation of similar complexes with the reagents studied, and some of the anions interfere by forming stronger complexes with titanium(IV) or by binding tetrazolium salts.

The use of ascorbic acid leads to a considerable increase in selectivity with respect to Fe(III), Cr(III), and Al(III) on the extraction of Ti—NC—TV. On the extraction of Ti—NC—INT it was found that the quantity of Al(III) masked by H_2PO_4^- was ten-fold greater than the one given in Table 3.

The method described was used for developing 10 parallel samples from each of two aluminium alloys. The results are given in Table 4.

The method we propose is suitable for routine work because the time for the analysis is short, the reagents are available and no preliminary separation of the macrocomponents is needed.

CONCLUSION

Our studies indicate that 4-nitrocatechol is a better chelate-forming reagent for titanium(IV) than pyrocatechol because of its stability against oxidation. Tetrazolium salt with naphthyl radical (TV) improves

Table 3. Effect of Diverse Ions in the Determination of $\rho(\text{Ti}) = 9.80 \mu\text{g cm}^{-3}$ with 4-Nitrocatechol and Tetrazolium Salts in 10 cm^3 of Chloroform

Ions	Amount m_i (added)/ μg	$m(\text{Ti})$, found as Ti—NC—INT/ μg	Amount m_i (added)/ μg	$m(\text{Ti})$, found as Ti—NC—TV/ μg
H ₂ PO ₄ ⁻	4800	9.80	1900	9.90
Cl ⁻	3500	9.67	525	10.10
Ascorbate	1760	9.57	2640	9.60
Cu ²⁺	998	10.10	1490	9.59
NO ₃ ⁻	620	9.80	316	9.78
Acetate	590	10.10	88	10.20
EDTA	336	10.03	1680	9.40
Cd ²⁺	200	9.77	300	9.76
F ⁻	190	9.90	95	9.69
Complexone IV	180	9.61	90	9.80
Zn ²⁺	110	9.70	2320	9.50
Mn ²⁺	100	9.85	50	9.41
Fe ³⁺	100	9.50	995	10.09
Al ³⁺	100	9.73	500	9.53
Br ⁻	80	9.65	80	9.69
Ni ²⁺	20	10.10	1460	10.00
Tartrate	10	interferes	10	interferes
Citrate	10	interferes	10	interferes
Mo(VI)	10	interferes	520	9.60
W(VI)	10	interferes	55	10.10
Nb(V)	10	interferes	10	interferes
V(V)	10	interferes	10	interferes
CNS ⁻	100	interferes	100	interferes

Table 4. Determination of Titanium in Aluminium Alloys

Sample	Recommended value/%	Obtained by present method/%	Obtained by the ICP-method/%
A*	0.06	0.058 ± 0.0024 $s_r = 1.05 \%$	0.058 $s_r = 7.3 \%$
B**	0.03	0.03 ± 0.0021 $s_r = 1.0 \%$	0.034 $s_r = 2.7 \%$

* w_i (other components): 2 % Cu; 8 % Mg; 7 % Zn; 0.6 % Mn; 0.25 % Cr.** w_i (other components): 4.5 % Cu; 2.5 % Mg; 0.8 % Mn.

the photometric and extraction characteristics of the ion-associate of titanium(IV) and in this way makes it applicable to the determination of a low content of titanium in aluminium alloys.

REFERENCES

- Bishop, E. (Editor), *Indicators*. Vol. 1. Pergamon Press, Oxford, 1972.
- Konopik, N. and Wimmer, G., *Monatsh. Chem.* 93, 1409 (1963).
- Busev, A. I. and Karyakina, Z. P., *Zh. Anal. Khim.* 22, 1506 (1967).
- Nazarenko, V. A., Lebedeva, N. V., and Vinarova, L. I., *Zh. Neorg. Khim.* 15, 2990 (1970); *Zh. Anal. Khim.* 27, 128 (1972).
- Nazarenko, V. A., Vinarova, L. I., Lebedeva, N. V., and Lyakh, R. A., *Ukr. Khim. Zh.* N 12, 1325 (1977).
- Sommer, L. and Bartůšek, M., *Folia Fac. Nat. Univ. Brun.* 7, 24 (1966).
- Nazarenko, V. A., Poluektova, E. N., and Shitareva, G. G., *Zh. Anal. Khim.* 28, 101 (1973).
- Antonovitch, V. P., Vinarova, L. I., Ivanova, E. S., and Stoyanova, I. V., *Zh. Anal. Khim.* 49, 80 (1989).
- Havelkova, L. and Bartůšek, M., *Collect. Czech. Chem. Commun.* 33, 385 (1968).
- Alexandrov, A. and Kostova, S., *Nauch. Tr. PU, Khimiya* 19, 15 (1981).
- Alexandrov, A., Kostova, S., and Navratyl, O., *Nauch. Tr. PU, Khimiya* 21, 15 (1983).
- Kostova, S., Alexandrov, A., and Ilieva, I., *Nauch. Tr. PU, Khimiya* 27, 67 (1989).
- Dimitrov, A. and Alexandrov, A., *Anal. Laboratory* 4, 172 (1995).
- Dimitrov, A. and Kostova, S., *Chem. Ind. (Bulg.)* 70, N3—4, 88 (1999).
- Kostova, S., Alexandrov, A., and Grivova, M., *Nauch. Tr. PU, Khimiya* 27, 79 (1989).
- Alexandrov, A., *Tetrazolium salts for solvent extraction of elements as ion-association complexes*. Univ. des Saarlandes, Saarbrücken, 1984.
- Agrawal, Y. K. and Jonh, K. T., *Analyst* 110, 57 (1985).

18. Busev, A. I., Tiptsova, V. G., and Ivanov, V. M., *Rukovodstvo po analiticheskoi khimii redkikh elementov*. Khimiya, Moscow, 1978.
19. Nabivanets, B. I. and Lukachina, V. V., *Ukr. Khim. Zh.* 30, 1123 (1964).
20. Bulatov, M. I. and Kalinkin, I. P., *Prakticheskoe rukovodstvo po fotometricheskim metodam*. Khimiya, Leningrad, 1976.
21. *Nouveau traité de chimie minérale* (publ. sous la direction de P. Pascal), Vol. 9, p. 177. Masson, Paris, 1963.
22. Linden, W. E., Boef, G., and Den, A., *Anal. Chim. Acta* 37, 179 (1967).
23. *Comp. Inorg. Chem.*, Vol. 3, p. 377. Pergamon Press, Oxford, 1973.
24. Likussar, W. and Boltz, P., *Anal. Chem.* 43, 1265 (1971).